

SOLID-STATE PHYSICS

When is a metal not a metal?

Steven C. Erwin

When it's an insulator, of course. Materials that should in theory conduct electricity — but don't — are well known, but the anomalous behaviour of one material has caused particular head-scratching.

Every student knows the difference between a metal and an insulator: one conducts electricity and the other doesn't. Things get more interesting if you ask how this difference arises. Although the question is disarmingly simple, a rigorous answer was not available until about 1930, when Felix Bloch and Alan Wilson used the new quantum mechanics to create a theory that distinguished metals from insulators^{1,2}. The spectacular success of this 'band theory of solids', as it is now known, has made it a cornerstone of the modern theory of solids.

In a few glaring cases, however, band theory doesn't get it right: the materials known as Mott insulators, for instance, are experimentally insulating, yet band theory firmly insists they are metallic. Writing in *Physical Review Letters*, Cortés and colleagues³ take a fresh look at one such material — a germanium surface with a layer of adsorbed tin atoms — that has been puzzling theorists and experimentalists alike. Despite expectations based on analogy with similar materials, previous experiments on this system had failed to establish it as a Mott insulator. The results of Cortés *et al.* finally put this piece of the puzzle into place.

Exceptions to band theory provide fertile soil for testing new ideas about the behaviour of electrons in solids. Perhaps no one contributed more than Nevill Mott, a 1977 Nobel laureate in physics. Mott pointed out that the central approximation of band theory — that each electron moves independently, feeling the effects of the others only on the average — would fail badly in certain circumstances⁴. Armed with this realization, physicists could finally begin to understand those materials that owe their insulating nature to correlations in the motions of different electrons. These correlations arise from nothing more than the classical Coulomb repulsion between particles of like charge. But they can be decisive in materials in which the two competing tendencies of electrons are already in delicate balance: the desire to be spatially localized to minimize Coulomb repulsion, and the need to be delocalized to minimize the cost in kinetic energy from spatial confinement.

In bulk materials, the tendency to delocalize — and so conduct — usually prevails, because the freedom offered by three dimensions is greater than the Coulomb penalty. Not so at the surfaces of semiconductors, where electrons are effectively confined to two

dimensions (Fig. 1). Indeed, Mott insulators have been created over the past decade on the surfaces of many common semiconductors, including silicon carbide, gallium arsenide and even silicon itself. In most cases, adsorbed dopant atoms were used to tune the number of electrons to the point where band theory would predict a metal. When the evidence showed otherwise, Mott's electron correlations were a natural suspect.

Despite the occasional failure, Bloch–Wilson band theory still provides a useful language for understanding even those materials it gets wrong. Electrons in crystalline solids cannot have arbitrary energies, nor can they all have the same energy. Instead, the specific arrangement of atoms within the solid dictates the ranges of allowed energies — the

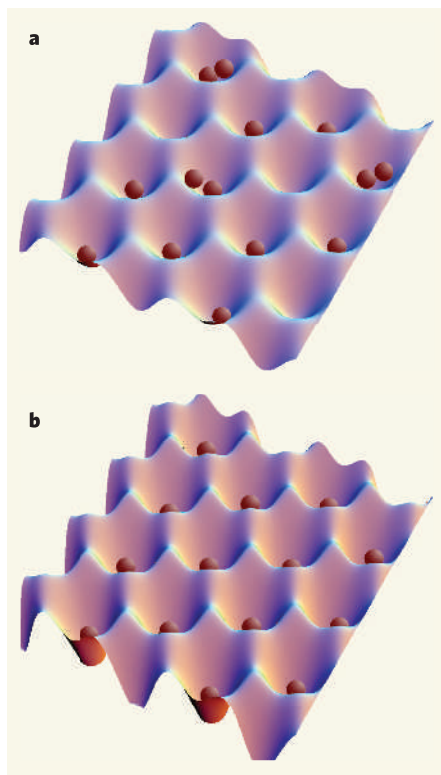


Figure 1 | Metal-insulator transition. **a**, The regular potential wells of a normal metallic state of a material with, on average, one electron per atom. **b**, If the confining potential is a little stronger (deeper wells), electrons find it harder to delocalize and so do not conduct — despite what the band theory of solids predicts. The material is a Mott insulator, such as the tin-covered germanium investigated by Cortés and colleagues³.

'bands' of band theory. The electrons must occupy the available bands sequentially, starting with the energetically lowest and proceeding upwards. Each band can accommodate two electrons of opposite spin. It follows that if the solid (more properly, one unit cell of the solid) contains an odd number of electrons, then at least one band must be incompletely filled. Such a material is guaranteed to be metallic within band theory.

The experimental search for surfaces meeting these conditions, but nonetheless exhibiting insulating behaviour, began in earnest in the 1990s. In one classic experiment, a Mott insulator was engineered on a silicon surface by first depleting its electrons using implanted boron. Then potassium was adsorbed until just enough electrons were supplied to meet the Bloch–Wilson criterion for a metal⁵. But data from photoemission spectroscopy (which uses light to eject electrons from a material and reveal their energy distribution) showed a gap between filled and empty bands. This contradiction with band theory provided strong evidence, eventually confirmed theoretically⁶, that the potassium-covered silicon surface is a Mott insulator.

A similar strategy was also applied to the surface of germanium, but with important differences. Instead of the boron–potassium combination, a single overlayer of lead was used to supply the same number of electrons. When this lead–germanium system was cooled below 100 kelvin, a small energy gap appeared, but accompanied by a new feature: a periodic, rumpling distortion of the lead overlayer⁷. When tin atoms (with the same number of valence electrons as the lead atoms) were added instead, the same rumpling was found, but the gap was mysteriously absent⁸. It has been persuasively argued⁹ that the rumpling seen at low temperatures in both systems is really the freezing of a vibrational mode in which, at higher temperatures, the tin atoms undergo rapid up–down oscillations. But the larger question — why the tin–germanium system seemed not to be a Mott insulator — remained unresolved.

Cortés and colleagues' contribution³ to the story is twofold. First, they establish that tin-covered germanium is indeed a Mott insulator, but only at very low temperatures. Second, they present angle-resolved photoemission data that give an especially detailed picture of the metal–insulator transition, adding weight to the earlier findings in related two-dimensional systems. Their primary evidence consists of photoemission spectra, taken at temperatures of 12 and 140 kelvin, that simultaneously measure the energy and momentum distribution of electrons. At the lower temperature the spectra show the opening of a textbook insulating gap. The authors buttress this result with a second, surprising, finding: at 12 kelvin, the rumpling distortion found in earlier experiments⁸ disappears and a uniform flat surface returns.

The observation of both phase transitions — electronic and structural — makes the picture particularly convincing. One final experiment measuring the 'inverse photoemission' spectrum (which reveals the distribution of empty states just above the gap) would clinch the case. For this, however, we must await improvements in resolution. In the meantime, the results of Cortés and colleagues restore a sense of order to our limited, but growing, understanding of Mott insulators on surfaces. Such an understanding may help to unravel other mysteries, from high-temperature superconductivity to ultracold atoms. And as the dimensions of electronic devices continue to shrink, Mott's theory may itself become the

new cornerstone for describing how electrons behave at the very smallest scales. ■
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CELL BIOLOGY

Skin care by keratins

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Keratin proteins perform several functions in skin cells, including those of providing mechanical support and protection against injury. But it seems they also have a more active part to play in healing wounds.

Like the musculoskeletal framework of humans or the steel-girder scaffolds of buildings, the intermediate filaments of the cytoskeleton shield cells from mechanical forms of injury^{1–3}. Intermediate filaments are made up of a large family of tissue-specific proteins, including desmin in muscle, neurofilaments in neurons and keratins in the epithelial cells that line organs such as the skin^{1–3}. Although intermediate filaments are well known for their protective properties, it seems that they may also have a role in damage repair. On page 362 of this issue, Kim *et al.*⁴ provide a direct mechanistic link between an increase in the expression of the gene for keratin K17 and the characteristic increase in protein synthesis and cell growth seen in the cells around wounds.

Wound healing involves the orchestration of numerous events in the recovering cells and those adjacent to them^{5,6}, such as cell growth, cell division and migration, and the upregulation of many genes — including those encoding several intermediate filament proteins (Fig. 1). In response to skin injury, for example, the cells surrounding the wound ramp up protein synthesis and enlarge to help seal the wound. In these cells, there is a rapid increase in the expression of several keratins (K6, K16 and K17)⁶.

Kim *et al.* began their study by pursuing their previous observation that injuries in mouse embryos lacking K17 show a striking delay in wound closure^{4,6}. They noted that the wound-edge cells from such embryos did not swell up as usual, and were about 40% smaller than those of normal embryos. Moreover,

these cells did not show the full protein-synthetic activity that typically accompanies cell growth. This initial link with cell growth led Kim *et al.* to explore the role of a regulatory enzyme called mammalian target of

rapamycin (mTOR). This enzyme can regulate cell growth and proliferation in other systems by controlling protein synthesis⁷. Kim *et al.* found that the activation of mTOR seen in normal cells is reduced in cells that lack K17.

So how does K17 affect mTOR signalling? The authors found that K17 binds to an adaptor protein called 14-3-3 σ , which belongs to the 14-3-3 protein family⁴. The 14-3-3 proteins bind to more than 100 other proteins, primarily at particular phosphoserine/phosphothreonine residues — that is, serine (Ser) and threonine (Thr) residues that have a phosphate group attached. One of their many functions is to regulate where their binding partners can reside in the cell⁸. Mutation of two sites on the K17 protein that looked likely to act as 14-3-3 binding motifs (Thr 9 and Ser 44) not only blocked the binding of K17 to 14-3-3, but also prevented the normal activation of mTOR and translocation of 14-3-3 from the nucleus to the cytoplasm in cultured cells. The investigators then went full circle by showing that reintroducing K17 into keratinocytes lacking K17 restored the movement of 14-3-3 from the nucleus to the cytoplasm, leading to stimulation of mTOR signalling and increased protein synthesis and cell size. By contrast, introducing K17 that was mutated at its 14-3-3-binding sites had no significant effect.

These findings directly implicate the keratin cytoskeleton in the regulation of protein synthesis and cell size, highlighting an overlooked non-mechanical function for skin keratins

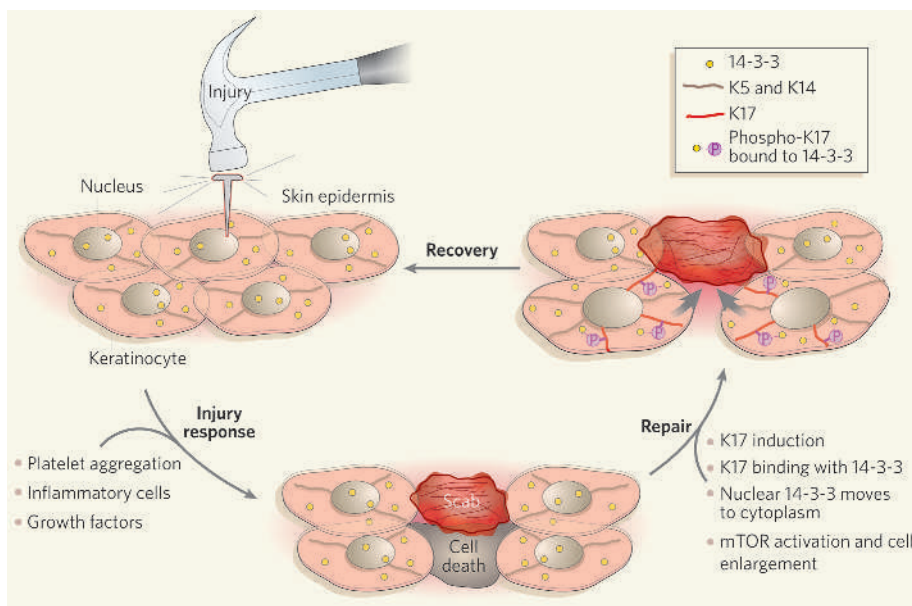


Figure 1 | The skin injury response. Injury to keratinocyte cells of the uppermost skin layer (epidermis), or injury to other tissues, triggers an elaborate repair response that includes possible bleeding and aggregation of platelet cells from the blood, scab formation, infiltration of inflammatory cells into the wound, and release of growth factors. The size, shape and adhesive properties of the keratinocytes surrounding the wound also change. These alterations result in part from changes in gene expression, including the induction of genes encoding the K6, K16 and K17 keratins. K17 probably undergoes phosphorylation, which results in binding of cytoplasmic K17 to the adaptor protein 14-3-3 and movement of nuclear 14-3-3 to the cytoplasm. As demonstrated by Kim *et al.*⁴, K17 induction and binding to 14-3-3 are key events for the activation of the mTOR signalling pathway and the ensuing stimulation of cell growth and migration.